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(54) Title of the Invention: METHOD OF PREPARING MODIFIED CELLULOSE  
ETHER

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## SPECIFICATION

1. Title of the Invention

Method of Preparing Modified Cellulose Ether

2. Claims

- (1) A method of preparing modified cellulose ether, the method being comprised of subjecting a cellulose ether sodium salt to electrodialysis so as to convert it to the acid form, followed by reaction with a base or salt.
- (2) The method of claim 1, wherein the membrane used in electrodialysis is an ion-exchange membrane or an ultrafiltration membrane.
- (3) The method of claim 1, wherein the solvent used in electrodialysis is an aqueous system or a mixed solvent system composed of a lower organic solvent having up to 3 carbons and water.
- (4) The method of claim 1, wherein the base or salt is a hydroxide, chloride, carbonate or lower carboxylate having up to 3 carbons of lithium, rubidium, calcium, magnesium aluminum or ammonium.

3. Detailed Description of the Invention

## Industrial Field of Use:

The present invention relates to a method of preparing modified cellulose ether.

## Prior Art:

Cellulose ethers are used as dispersing agents, thickeners, adhesives, protective colloids, and in other ways. In anionic cellulose ethers such as carboxymethyl cellulose (CMC), the ether groups serving as the substituents are generally in the form of sodium salts for reasons having to do with the ease of production or on account of physical property requirements such as water solubility.

However, as applications for cellulose ether continue to expand, there is felt to be a strong industrial need for what is referred to here as modified cellulose ether; that is, cellulose ether in which the counter ions for the anionic ether groups are metal ions other than sodium ions, or cations.

For example, the calcium salt of CMC is used as a disintegrating agent in pharmaceutical tablets, the lithium salt of CMC is employed in battery compositions, and the ammonium salt of CMC has applications in ceramic binders, gypsum clay and phosphor films. Hence, characteristics very different from those of the sodium salt form are employed in this way.

## Problems to be Solved by the Invention:

These modified cellulose ethers are prepared from the sodium salt form serving as the original ether by treatment in some way to eliminate the sodium, and conversion to another salt form. However, because the complete removal of sodium has not yet been achieved for reasons having to do with the production method, use of the calcium salt of CMC, for example, results in a deterioration in the tablet disintegrating ability.

Similarly, use of the ammonium salt of CMC weakens the sintering forces in a ceramic, rendering it fragile. Additional problems that arise include a deterioration in the electrical characteristics and a decline in the dielectric properties. Hence, the presence of the sodium salt of cellulose ether has a highly undesirable influence in [modified cellulose ether] applications.

To cite an example, the calcium salt of CMC is generally prepared by having calcium hydroxide, calcium chloride or the like act directly on the sodium salt of CMC, as described in, for example, Soviet Patent No. 553,253 and JP-A 60-38401 (1985). An essential drawback is that, as gelation proceeds, replacement of the sodium salt form with the calcium salt form becomes impossible. In another method, described in JP-A 60-47001 (1985), the sodium salt of CMC is first rendered into an acidic form using a mineral acid such as sulfuric acid or hydrochloric acid, then is acted upon by calcium hydroxide. In this latter method, during the process of acidification, for reasons such as the inevitable decline in the degree of polymerization of the cellulose chain, use must be made of a low-concentration acid. As a result, the reactivity decreases, in addition to which this method is influenced by the degree of ether group substitution or by the ionic strength. Hence, this method cannot be used on the sodium salts of strongly anionic cellulose ethers, such as high-degree-of-substitution cellulose ethers or sulfoethyl cellulose.

Moreover, in the method described in Soviet Patent No. 956,486 for the simultaneous treatment of cellulose with a mixed system composed of an etherizing agent and a calcium compound, because it is necessary to satisfy the conditions for both the etherizing reaction and for the reaction in which the ether group is rendered into a calcium salt, this approach has the drawback that the cellulose etherizing ratio is very low.

As noted above, what remains a problem in prior-art production methods is the residual presence of sodium components in the modified cellulose ether.

#### Objects of the Invention:

The present invention makes it possible to produce sodium salt-free modified cellulose ether by the entirely novel use of electrical energy to easily and completely eliminate sodium from the starting cellulose ether, and by having a base act on the resulting completely acidic cellulose gel.

#### Means for Resolving the Problems:

Accordingly, the present invention is directed at a method of preparing modified cellulose ether, the method being comprised of subjecting a cellulose ether sodium salt to electrodialysis so as to convert it to the acid form, followed by reaction with a base or salt.

#### Conditions Necessary to Constitute the Means:

"Cellulose ether sodium salt," as used herein, refers to a sodium salt of, for example, carboxymethyl cellulose (CMC), carboxymethyl cellulose (CEC), carboxymethylhydroxyethyl cellulose (CMHEC), carboxymethylhydroxypropyl cellulose (CMHPC), sulfoethyl cellulose (SEC), sulfopropyl cellulose (SPC), carboxymethyl-

sulfoethyl cellulose (CMSEC) and carboxymethylsulfopropyl cellulose (CMSPC). These cellulose ethers can be obtained by having a suitable etherizing agent act on the cellulose in the presence of sodium hydroxide. The present invention is not limited only to the use of purified product. For example, use can also be made of a crude product containing the low-molecular-weight salts which form as by-products of the process in which these cellulose ethers are produced.

In addition, "base" and "salt," as used herein, refer to the hydroxides, chlorides, carbonates or lower carboxylates having up to 3 carbons (e.g., formate, acetate) of, for example, lithium, rubidium, calcium, magnesium, aluminum or ammonia.

The "method of producing modified cellulose ether" according to the present invention refers to a method in which the above-described cellulose ether sodium salt is rendered into the acid form by electrodialysis, then is reacted with the above-mentioned base or salt.

The reference here to electrodialysis for converting the cellulose ether sodium salt to the acid form relates to the process of using an electrolytic cell divided into three compartments in which platinum electrodes are employed as both electrodes and ion-exchange membranes, ultrafiltration membranes or the like are used as the membranes to remove, in an aqueous system or a mixed solvent system composed of a lower organic solvent of up to three carbons and water, low-molecular-weight ions so as to form in the compartment between both membranes, a high-purity acid-type cellulose gel containing no low-molecular-weight ions, and especially no metal ions.

The acid-type cellulose gel thus prepared is then reacted with an aqueous solution of the above-mentioned base or salt in a suitable concentration so as to form an alkali salt other than a sodium salt. If the product formed is water-soluble, precipitation may be induced with a suitable organic solvent and purification effected with a water-containing organic solvent. On the other hand, if the product is water-insoluble, the precipitate is purified with water.

The "lower organic solvent of up to three carbons" used in a mixed solvent system with water refers to lower alcohols and ketones such as methanol, ethanol, 2-propanol and acetone. The mixing ratio (by weight) of the lower organic solvent and water is preferably within a range of 1:99 to 80:20.

#### Advantages of the Invention:

The inventive method of preparing modified cellulose ether can be expected to provide a number of excellent effects, including the following:

- (1) The modified cellulose ether contains no sodium.
- (2) The concentration of impurities in the modified cellulose ether is less than 0.01%, resulting in a very high product purity.
- (3) The modified cellulose ether shows substantially no decrease in the degree of polymerization.
- (4) The inventive method of preparation is low-polluting.

#### Examples:

Examples are given below by way of illustration. All percent in the examples are by weight.

Working Example 1

A 2% aqueous solution (700 g) of carboxymethyl cellulose sodium salt (Na-CMC; DS = 1.05; 2% aqueous solution viscosity at 25°C, 2700 mPa·s; viscosity values shown below are all aqueous solution viscosities of 2% solutions of sample at 25°C) was electrodialyzed in an electrolysis apparatus (model PAB 110-0.6; produced by Kikusui Electronics Corp.) comprising platinum plates as both electrodes and ultrafiltration membranes (manufactured by Toyo Soda Manufacturing Co., Ltd.; molecular cutoff, 300,000; the same applies below) as the dialysis membranes under stirring by applying a current of 0.55 A for 5 hours, thereby forming 170 g of water-insoluble acid-type CMC gel having a volatiles content of 88%.

This gel was placed in a "juicer" mixer containing 100 g of a 10% calcium acetate solution in water and stirred at room temperature, following which the precipitate was removed. In addition, the precipitate was purified three times with 300 g of water, following which it was dehydrated with methanol and dried at 105°C, giving 13.2 g of CMC calcium salt (Ca-CMC).

In this example, the viscosity of a 2% aqueous solution of Na-CMC obtained by dissolving the water-insoluble acid-type CMC in 5% aqueous NaOH was 2610 mPa·s.

Working Example 2

A 40% aqueous solution of 2-propanol (458 g) having a 4% concentration of sulfoethyl cellulose sodium salt (Na-SEC; DS = 0.86; viscosity, 378 mPa·s) was electrodialyzed in the same way as in Working Example 1, except that the membranes used were ion-exchange membranes (a cation-exchange membrane ("Asiplex" K-101, manufactured by Asahi Chemical Industry Co., Ltd.) at the cathode, and an anion-exchange membrane ("Asiplex" A-201, manufactured by Asahi Chemical Industry Co., Ltd.) at the anode; the same applies below), thereby giving 180 g of a water-soluble gel having a volatiles content of 91%. This gel was reacted at room temperature with 120 g of 10% magnesium acetate, following which 180 g of basic methanol was added, and the precipitate was removed. The precipitate was purified with a 80% solution of methanol in water, dehydrated with 80 g of methanol and dried at 105°C, giving 16.4 g of SEC magnesium salt (Mg-SEC).

Working Example 3

A water-insoluble gel having a volatiles content of 90% was prepared by the electrodialysis of 506 g of a 55% solution of methanol in water having a 2% concentration of Na-CMC (DS = 0.77; viscosity, 9700 mPa·s) in the same manner as in Working Example 1, except that the membrane used was an ion-exchange membrane. This gel was reacted at room temperature with 20 g of 10% ammonia water, following which 180 g of 99% 2-propanol was added to effect precipitation. This precipitate was purified three times with 60 g of 70% methanol and vacuum dried at 60°C, giving 9.8 g of CMC ammonium salt ( $\text{NH}_4\cdot\text{CMC}$ ).

\* Translator's Note: Unconfirmed spellings are enclosed in quotation marks.

In this example, the viscosity of a 2% aqueous solution of Na-CMC obtained by dissolving the water-insoluble acid-type CMC in 5% aqueous NaOH was 9400 mPa·s.

#### Working Example 4

A water-insoluble gel having a volatiles content of 85% was prepared by the electrodialysis of 1470 g of a 50% solution of methanol in water having a 2% concentration of Na-CMC (DS = 0.72; viscosity, 19700 mPa·s) in the same manner as in Working Example 1, except that the membrane used was an ultrafiltration membrane.

This gel was reacted at room temperature with 100 g of 10% aqueous lithium hydroxide, following which 99% 2-propanol was added to effect precipitation. This precipitate was purified three times with 300 g of an 85% solution of methanol in water and dried at 105°C, giving 27.4 g of CMC lithium salt (Li·CMC).

#### Working Example 5

A water-insoluble gel having a volatiles content of 92% was prepared by the electrodialysis of 680 g of a solution of methanol in water having a 4% concentration of Na-CMC (DS = 1.40; viscosity, 2300 mPa·s) in the same manner as in Working Example 1, except that the membrane used was an ion-exchange membrane.

This gel was reacted at room temperature with 2600 g of a basic 0.1% solution of aluminum acetate in water, thereby giving a white gel. This gel was purified three times with 300 g of water and dried at 105°C, giving 24.3 g of CMC aluminum salt (Al·CMC).

#### Working Example 6

A liquid paste prepared by dissolving 22.0 g of Na-CMSEC (CH groups, DS = 0.80; SE group, DS = 0.6) in 528 g of a 45% solution of 2-propanol in water was electrodialyzed in the same general manner as in Working Example 1, except that an ion-exchange membrane was used as the membrane.

The resulting gel was removed, reacted at room temperature with 125 g of a 10% solution of calcium acetate in water, then 200 g of 2-propanol was added, giving a white precipitate. This precipitate was purified twice with 350 g of an 80% solution of methanol in water, then dried at 105°C to give 20.9 g of Ca-CMSEC.

#### Working Example 7

Na-CMHEC (18.7 g; CM group DS = 0.80; HE group MS = 0.72) was dissolved in 515 g of 50% 2-propanol, and electrodialysis was carried out in much the same way as in Working Example 1, except that an ion-exchange membrane was used as the membrane.

The resulting gel was removed and reacted at room temperature with 115 g of a 10% solution of magnesium acetate in water, giving a white gel. This gel was purified three times with 300 g of an 80% solution of methanol in water, then dried at 105°C to give 17.2 g of Mg-CMHEC.

#### Comparative Example 1

Na-CMC (14.0 g; DS = 1.05; viscosity, 2700 mPa·s) was acidified by the addition thereto of 18% H<sub>2</sub>SO<sub>4</sub> (280 g), followed by 5 hours of stirring at 55°C.

Excess acid was separated off, following which 700 g of water was added and deacidification treatment was carried out. This operation was repeated another ten times to give a water-insoluble acid-type CMC. Next, the acid-type CMC was placed in a "juicer" mixer containing a 10% solution of calcium acetate in water and vigorously stirred to give a precipitate. This product was purified ten times with 300 g of water and dried at 105°C to give 10.1 g of Ca-CMC.

In this comparative example, the viscosity of a 2% aqueous solution of Na-CMC obtained by dissolving the water-insoluble acid-type CMC in 5% aqueous NaOH was 1300 mPa·s.

#### Comparative Example 2

Na-SEC (91.6 g; DS = 0.86) was dispersed in 2824 g of a 2% solution of magnesium acetate in water and the mixture was stirred at room temperature for 5 hours. Next, 11300 g of 2-propanol was added to the resulting gel-like liquid, giving a precipitate. This precipitate was purified with 800 g of a 80% solution of methanol in water, following which the same operation was repeated another ten times and drying was carried out at 105°C, giving 44.3 g of Mg-SEC.

#### Comparative Example 3

Na-CMC (50.6 g; DS = 0.77; viscosity, 9700 mPa·s) was acidified by the addition thereto of 18% H<sub>2</sub>SO<sub>4</sub> (1108 g), followed by 4 hours of stirring at 50°C. Excess acid was separated off, following which 2500 g of water was added and deacidification treatment was carried out. This operation was repeated another seven times to give a water-insoluble acid-type CMC. The acid-type CMC was then reacted with 150 g of 10% ammonia water, following which 630 g of 2-propanol was added to give a precipitate. This precipitate was purified ten times with 500 g of water, then vacuum dried at 60°C to give 33.7 g of NH<sub>4</sub>-CMC.

In this comparative example, the viscosity of a 2% aqueous solution of Na-CMC obtained by dissolving the water-insoluble acid-type CMC in 5% aqueous NaOH was 5400 mPa·s.

The results of the above working examples of the invention and comparative examples are presented in Table 1 below.

Table I

	Starting material		Modified cellulose ether				
	Form	DS	Form	Bonded cations (%)	Bonded sodium (%)	Sulfate ions (%)	Absorption (%)
Working Example 1	Na-CMC	1.05	Ca-CMC	Ca, 8.19	0.002	0	96.0
Working Example 2	Na-SEC	0.86	Mg-SEC	Mg, 3.81	0.007	0	93.1
Working Example 3	Na-CMC	0.77	NFL-CMC	N, 4.91	0.015	0	97.3
Working Example 4	Na-CMC	0.72	Li-CMC	Li, 2.40	0.008	0	98.4
Working Example 5	Na-CMC	1.40	Al-CMC	Al, 3.55	0.007	0	96.7
Working Example 6	Na-CMSEC	CM, 0.47 SE, 0.61	Ca-CMSEC	Ca, 7.14	0.004	0	97.3
Working Example 7	Na-CMHEC	CM, 0.80 HE, 0.72	Mg-CMHEC	Mg, 3.62	0.003	0	95.4
Comparative Example 1	Na-CMC	1.05	Cr-CMC	Ca, 7.49	0.287	1.87	69.5
Comparative Example 2	Na-SEC	0.86	Mg-SEC	Mg, 3.15	1.469	0	49.7
Comparative Example 3	Na-CMC	0.77	NH <sub>4</sub> -CMC	N, 3.91	0.632	2.75	65.4

\*In the DS column for Working Example 6, CM stands for the degree of carboxymethyl group substitution, and SE stands for the degree of sulfoethyl group substitution.

In the DS column for Working Example 7, CM stands for the degree of carboxymethyl group substitution, and HE stands for the hydroxyethyl group molar degree of substitution.

\*\*The lithium, calcium, magnesium and aluminum contents were determined by atomic absorption spectroscopy, and the nitrogen content was determined by the Kjeldahl method.

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